



THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of : Confirmation No. 6903  
Kenji ISHII et al. : Attorney Docket No. 2005\_2064A  
Serial No. 10/562,876 : Group Art Unit 1796  
Filed December 29, 2005 : Examiner Liam J. Heincer

PROCESS FOR THE PRODUCTION OF  
BIFUNCTIONAL PHENYLENE ETHER  
OLIGOMER COMPOUND

DECLARATION UNDER 37 CFR 1.132

Atsushi HIRASHIMA declares:

That his education and professional background are as follows:

He graduated from Saitama University, the Organic Synthetic Chemistry Course of the Department of Chemistry in the Faculty of Science in March 1990, joined Mitsubishi Gas Chemical Company, Inc., in April 1990, was attached to Corporate Research Laboratory, and was attached to Tokyo Research Laboratory in 2005, where he has been and is engaged in the study and development of basic technologies of oligomers of phenylene ethers since 2005:

That he has conducted tests as set forth in the attached Experimental Report to demonstrate that an amine adduct generates when a secondary amine having no bulky substituent is used:

That from these tests he concludes that amine adducts existed in the phenylene ether oligomers obtained by jointly using di-n-butylamine, which is a secondary amine having no bulky substituent.

He further declares that all statements made herein of his own knowledge are true, and that all statements on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

The 20th day of October, 2008

Atsushi Hirashima

Atsushi HIRASHIMA

## Experimental Report

### 1. Purpose of Experiments

To demonstrate that an amine adduct generates when a secondary amine having no bulky substituent, which is excluded by the present invention, is used.

### 2. Supplemental Experiments

Polymerization was carried out by jointly using as an amine catalyst di-n-butylamine (DBA), which is a secondary amine having no bulky substituent, in addition to two kinds of amines, which are essential in the present invention.

#### Supplemental Experiment 1

A longitudinally long reactor having a volume of 12 liters and equipped with a stirrer, a thermometer, an air-introducing tube and baffleplates was charged with 1.95 g (8.7 mmol) of  $\text{CuBr}_2$ , 0.64 g (3.7 mmol) of N,N'-di-t-butylethylenediamine, 9.65 g (95.4 mmol) of n-butyldimethylamine, 12.28 g (95.0 mmol) of di-n-butylamine, 0.71 g (1.7 mmol) of tri-n-octylmethyl ammonium chloride and 2,100 g of toluene. The components were stirred at a reaction temperature of 40 °C. A mixed solution (bivalent phenol of the formula (2) of the present specification : monovalent phenol of the formula (3) of the present specification in molar ratio = 1 : 5) was obtained by dissolving 129.8 g (0.48 mol) of 2,2',3,3',5,5'-hexamethyl-(1,1'-biphenyl)-4,4'-diol (to be referred to as "HMBP" hereinafter), 293.2 g (2.40 mol) of 2,6-dimethylphenol, 1.95 g (8.7 mmol) of  $\text{CuBr}_2$ , 0.64 g (3.7 mmol) of N,N'-di-t-butylethylenediamine and 29.45 g (291.0 mmol) of n-butyldimethylamine in 2,300 g of methanol in advance. The mixed solution was dropwise added to the mixture in the reactor over 230 minutes while carrying out bubbling with 5.2L/min of a nitrogen-air mixed gas having an oxygen concentration of 8 %, and stirring was carried out. After the completion of the addition, 1,500 g of water in which 19.84 g (43.9 mmol) of tetrasodium ethylenediamine tetraacetate tetrahydrate was dissolved was added to the stirred mixture to terminate the reaction. An aqueous layer and an organic layer were separated. Then, the organic layer was washed with 1.0 N hydrochloric acid aqueous solution and then with pure water. The thus obtained

solution was concentrated with an evaporator and then dried under a reduced pressure, to obtain 414.3 g of a phenylene ether oligomer compound. The phenylene ether oligomer compound had a number average molecular weight ( $M_n$ , hereinafter) of 1,250, a weight average molecular weight ( $M_w$ , hereinafter) of 1,830,  $M_w/M_n$  of 1.46 and a hydroxyl group equivalent of 575. Unreacted HMBP was 2.7 % and unreacted 2,6-dimethylphenol was 0.1 %. A peak corresponding to di-n-butylamine was detected in its  $^1\text{H-NMR}$  measurement. From the integration ratio of the peak (0.93 ppm) of its methyl group, it was confirmed that an amine adduct was present in an amount of 14 %.

## Supplemental Experiment 2

A longitudinally long reactor having a volume of 12 liters and equipped with a stirrer, a thermometer, an air-introducing tube and baffleplates was charged with 0.98 g (4.4 mmol) of  $\text{CuBr}_2$ , 0.44 g (2.6 mmol) of  $N,N'$ -di-t-butylethylenediamine, 10.73 g (106.0 mmol) of n-butyltrimethylamine, 0.71 g (5.5 mmol) of di-n-butylamine, 0.71 g (1.7 mmol) of tri-n-octylmethyl ammonium chloride and 2,600 g of toluene. The components were stirred at a reaction temperature of 40 °C. A mixed solution (bivalent phenol of the formula (2) : monovalent phenol of the formula (3) in molar ratio = 1 : 5) was obtained by dissolving 129.8 g (0.48 mol) of HMBP, 293.2 g (2.40 mol) of 2,6-dimethylphenol, 2.93 g (13.1 mmol) of  $\text{CuBr}_2$ , 0.89 g (5.2 mmol) of  $N,N'$ -di-t-butylethylenediamine, 21.45 g (212.0 mmol) of n-butyltrimethylamine and 1.41 g (10.9 mmol) of di-n-butylamine in 2,300 g of methanol in advance. The mixed solution was dropwise added to the mixture in the reactor over 230 minutes while carrying out bubbling with 5.2L/min of a nitrogen-air mixed gas having an oxygen concentration of 8 %, and stirring was carried out. After the completion of the addition, 1,500 g of water in which 34.09 g (75.4 mmol) of tetrasodium ethylenediamine tetraacetate tetrahydrate was dissolved was added to the stirred mixture to terminate the reaction. An aqueous layer and an organic layer were separated. Then, the organic layer was washed with 1.0 N hydrochloric acid aqueous solution and then with pure water. The thus obtained solution was concentrated with an evaporator and then dried under a reduced pressure, to obtain 409.5 g of a phenylene ether oligomer compound. The phenylene ether oligomer

compound had Mn of 1,330, Mw of 2,100, Mw/Mn of 1.58 and a hydroxyl group equivalent of 685. Unreacted HMBP was 1.9 % and unreacted 2,6-dimethylphenol was less than 0.1 %. A peak corresponding to di-n-butylamine was detected in its <sup>1</sup>H-NMR measurement. From the integration ratio of the peak (0.89 ppm) of its methyl group, it was confirmed that an amine adduct was present in an amount of 5 %.

### Supplemental Experiment 3

A longitudinally long reactor having a volume of 12 liters and equipped with a stirrer, a thermometer, an air-introducing tube and baffleplates was charged with 3.90 g (17.5 mmol) of CuBr<sub>2</sub>, 0.85 g (4.9 mmol) of N,N'-di-t-butylethylenediamine, 10.41 g (102.9 mmol) of n-butyltrimethylamine, 8.22 g (63.5 mmol) of di-n-butylamine, 0.71 g (1.7 mmol) of tri-n-octylmethyl ammonium chloride and 2,600 g of toluene. The components were stirred at a reaction temperature of 40 °C. A mixed solution (bivalent phenol of the formula (2) : monovalent phenol of the formula (3) in molar ratio = 1 : 5) was obtained by dissolving 129.8 g (0.48 mol) of HMBP, 293.2 g (2.40 mol) of 2,6-dimethylphenol, 1.72 g (10.0 mmol) of N,N'-di-t-butylethylenediamine, 20.78 g (205.4 mmol) of n-butyltrimethylamine and 16.35 g (126.5 mmol) of di-n-butylamine in 2,300 g of methanol in advance. The mixed solution was dropwise added to the mixture in the reactor over 95 minutes while carrying out bubbling with 3.5L/min of air, and stirring was carried out. During this addition, 3.5 L/min of a nitrogen gas was flown in gaseous phase. After the completion of the addition, 1,500 g of water in which 19.84 g (43.9 mmol) of tetrasodium ethylenediamine tetraacetate tetrahydrate was dissolved was added to the stirred mixture to terminate the reaction. An aqueous layer and an organic layer were separated. Then, the organic layer was washed with 1.0 N hydrochloric acid aqueous solution and then with pure water. The thus obtained solution was concentrated with an evaporator and then dried under a reduced pressure, to obtain 407.2 g of a phenylene ether oligomer compound. The phenylene ether oligomer compound had Mn of 1,200, Mw of 1,600, Mw/Mn of 1.33 and a hydroxyl group equivalent of 605. Unreacted HMBP was 2.3 % and unreacted 2,6-dimethylphenol was 0.1 %. A peak corresponding to di-n-butylamine was detected in its <sup>1</sup>H-NMR measurement. From the integration ratio of the peak (0.89

ppm) of its methyl group, it was confirmed that an amine adduct was present in an amount of 18 %.

Table 1 shows a summary of the results obtained in the Supplemental Experiments 1 - 3. In addition, Table 1 also shows the results of Examples and Comparative Examples of the present specification, which are related to the Supplemental Experiments 1 - 3.

Table 1 Results of Experiments

	Amount of catalysts [mmol] Divisional molar ratio (1) CuBr <sub>2</sub> (2) DtBEDA (3) BDMA (4) DBA		Supply time of raw materials [min]	Maturation time [min]	Remaining monomer HMBP [wt%]	2,6-X [wt%]
Supplemental Experiment 1	(1) 17.4 (2) 7.4 (3) 386.4 (4) 95	(1) 50:50 (2) 50:50 (3) 25:75 (4) 100:0	230	0	2.7	0.1
Example 4 of the present specification	(1) 17.4 (2) 7.4 (3) 386.4 (4) 0	(1) 50:50 (2) 50:50 (3) 50:50 (4)	230	0	0.5	<0.1
Supplemental Experiment 2	(1) 17.5 (2) 7.8 (3) 318 (4) 16.4	(1) 25:75 (2) 33:67 (3) 33:67 (4) 33:67	230	0	1.9	<0.1
Example 1 of the present specification	(1) 17.5 (2) 7.5 (3) 386.4 (4) 0	(1) 25:75 (2) 25:75 (3) 25:75 (4)	230	0	1.5	0.1
Comparative Example 3 of the present specification	(1) 17.4 (2) 7.4 (3) 96.6 (4) 0	(1) 50:50 (2) 100:0 (3) 100:0 (4)	230	0	7.2	1.6
Supplemental Experiment 3	(1) 17.5 (2) 14.9 (3) 308.3 (4) 190	(1) 100:0 (2) 33:67 (3) 33:67 (4) 33:67	95	0	2.3	0.1
Example 7 of the present specification	(1) 17.4 (2) 7.4 (3) 386.4 (4) 0	(1) 50:50 (2) 50:50 (3) 50:50 (4)	95	0	0.8	<0.1
Comparative Example 1 of the present specification	(1) 17.4 (2) 14.8 (3) 308.4 (4) 190.6	(1) 100:0 (2) 33:67 (3) 33:67 (4) 33:67	230	0	4.6	0.9

DtBEDA: N,N'-di-t-butylethylenediamine, BDMA: n-butyldimethylamine, DBA: di-n-butylamine, HMBP: 2,2',3,3',5,5'-hexamethyl-(1,1'-biphenyl)-4,4'-diol, 2,6-X: 2,6-dimethylphenol

Bivalent phenol: monovalent phenol in molar ratio = 1:5 in all of

Supplemental Experiments, Examples and Comparative Examples.  
In Supplemental Experiment 3 and Example 7 of the present specification, the reaction was conducted under air. In the others, the reaction was conducted under an atmosphere having an oxidation concentration of 8 %.

Table 1 (Continued)

	Mn Number average molecular weight	Molecular weight Mw Weight average molecular weight	Mw/Mn Molecular weight distribution	OH equivalent [g/eq]	Amount of amine adduct [%]
Supplemental Experiment 1	1,250	1,830	1.46	575	14
Example 4 of the present specification	930	1,470	1.58	470	Not Detected
Supplemental Experiment 2	1,330	2,100	1.58	685	5
Example 1 of the present specification	900	1,420	1.58	455	Not Detected
Comparative Example 3 of the present specification	870	1,380	1.59	440	Not Detected
Supplemental Experiment 3	1,200	1,600	1.33	605	18
Example 7 of the present specification	920	1,460	1.59	465	Not Detected
Comparative Example 1 of the present specification	930	1,370	1.47	470	22

### 3. Conclusion

From the above results of the Supplemental Experiments, it is obvious that the amine adducts existed in the phenylene ether oligomers obtained by jointly using DBA and that no amine adduct generated in the phenylene ether oligomers obtained without the use of DBA in the Examples of the present specification.